Effect of plasticizer on the cracking of ceramic green bodies in gelcasting

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Gelcasting has attracted great interest in ceramic industries due to its potential to form complex ceramic parts from a wide range of ceramic materials [1–4]. It has been demonstrated that the process can greatly improve the homogeneity and strength of the green bodies and the mechanical properties after sintering [5–8]. The main steps of gelcasting are as follows [9]. First, the ceramic powder (e.g., alumina or silicon nitride, etc.) is thoroughly mixed with small quantities of gel initiators, catalysts, monomers, cross-linkers and sintering additives to form a homogeneous suspension with high solid volume loading and low viscosity. Second, the suspension is cast into a hot mold to form a gel network by *in-situ* polymerization that holds all the ceramic particles. Finally, the green bodies are demolded, dried and sintered at a high temperature.

The gelation process is very sensitive to the temperature. The suspension solidifies faster near the mold surface where the temperature is initially higher. The non-uniform gelation will lead to the development of internal stress in the green body. It is noted that cracking in subsequent drying or de-bindering process is usually a consequence of the internal stress initiated in the forming process. The larger the ceramics parts, the more harmful this stress. Therefore, it is of great importance to minimize the internal stress in the green bodies during the gelcasting of large size ceramic parts.

As is well known in plastics industries, plasticizers are usually added to a polymer to reduce the elastic modulus and improve the flexibility of the polymer [10]. Inspired by this technique, various plasticizing agents are added to the suspension in gelcasting in order to reduce the elastic modulus of the gel network and reduce the internal stress in the green body. The effects of the plasticizers on the cracking of the green bodies and the optimum amount are herein investigated.

The following raw materials were used: deionized water with a conductivity of 1.02 μS·cm^{-1}, acrylamide (AM) as monomer, methylenebisacrylamide (MBAM) as cross-linker, $(NH_4)_2S_2O_8$ as initiator, N,N,N′,N′-tetraethylmethylenediamine (TEMED) as catalyst and ammonium citrate as dispersant. Al_2O_3 powder is commercially pure (produced by Xinyuan Alumina Plant of Henan, China). Three plasticizers were used: glycerine, polyethylene glycol [$-(CH_2-CH_2-O)_n-$] (PEG, average molecular weight of 6000) and polyvinyl pyrrolidone (PVP-K30) with structure as shown in Fig. 1.

A premix solution with AM (14 wt.%) and MBAM (0.6 wt.%) was prepared in the deionized water. The Al_2O_3 powder was dispersed into the premix solution at 50 vol.% solid loading. In order to obtain a low viscosity, 1 wt.% ammonium citrate was also added to the solution as dispersant. Each of glycerine, PEG and PVP was added as plasticizer respectively. The suspension was subjected to ball milling for 24 h, thus a low viscosity was obtained. The green bodies were produced by casting 100 ml of each suspension into a 150 ml beaker (the diameter was about 5.6 cm). They were dried for 48 h at room temperature and then put into an oven at 80 °C until constant weight was attained, and debinded for 40–50 h from room temperature to 600 °C. The cracks in the ceramic green bodies were monitored using a short focal distance digital camera. Test bars of the dry green bodies were prepared with dimensions of 6.5 × 5.5 × 42 mm for the measurements of the flexural strength and elastic modulus.

Fig. 2 shows the cracks in all of the Al_2O_3 green bodies containing glycerine in the suspension. The observations confirm that glycerine is not an effective plasticizer for this system. This is because the glycerine molecule is small compared with AM and MBAM polymer so that the effect on the intermolecular force in the gel network is limited.

Fig. 3 shows that the Al_2O_3 green bodies with PEG $\geq$1 wt.% are free of cracks implying that the internal stress is reduced with the addition of PEG. This can be explained by the thermodynamic theory of polymers [11]. When a polar plasticizer such as PEG is added to a polar polymer, the polar groups of the plasticizer will interact with the polar groups of the polymer molecules. Therefore, polar connections between the polymer molecules will be destroyed and the interaction force between the polymer molecules will decrease. Consequently, the flexibility of the gel network

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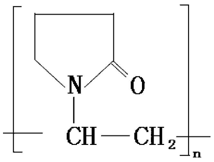

Figure 1 The molecular structure unit of PVP.

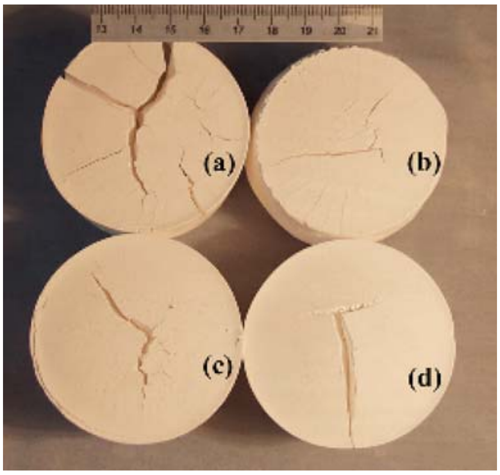

Figure 2 The Al_2O_3 green bodies adjusted by various amount of glycerine in the premix solution: (a) 2 vol.%, (b) 4 vol.%, (c) 6 vol.% and (d) 8 vol.%.

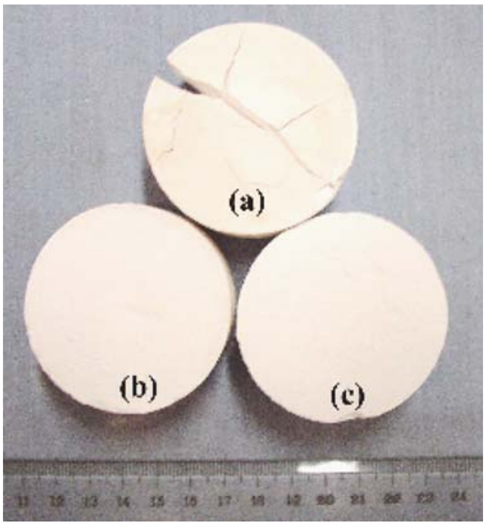

Figure 3 The Al_2O_3 green bodies adjusted by various amount of PEG in the Al_2O_3 powder: (a) 0.5%, (b) 1% and (c) 1.5%.

of the green body will be improved and the internal stress will be lowered.

The addition of PVP has an opposite effect. All the green bodies prepared with PVP have cracks after debinding as shown in Fig. 4. It is well known that PVP molecule has a lactam group with a strong polarity (c.f. Fig. 1) so that it is compatible with polar groups such as hydroxyl, amino or carboxyl group. On the other hand, PVP is compatible with oil groups owing to the non-polar methylene and sub-methylene groups in the molecule ring [12]. Therefore, PVP molecules are able to couple with both the polar and non-polar groups of poly-acrylamide molecules preventing the polymer chains from moving freely. This strengthens the gel network in gelcasting process and hence increases the internal stress in the green bodies. The green bodies are more prone to cracking.

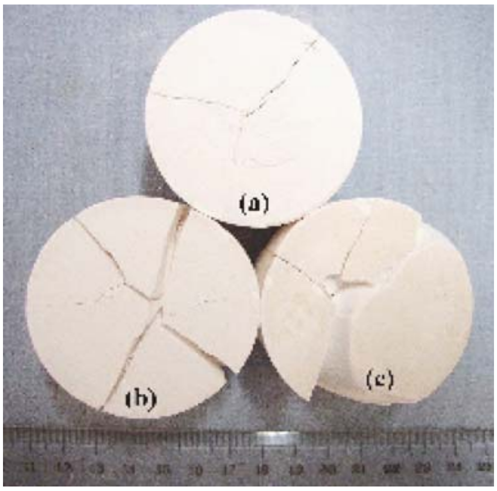

Figure 4 The Al_2O_3 green bodies adjusted by various amount of PVP in the Al_2O_3 powder: (a) 0.5%, (b) 1% and (c) 1.5%.

The vitrification point is widely used as an indication of the intermolecular interaction in polymer science. The higher the intermolecular attraction, the higher the vitrification point. The vitrification point T_g of the polymer modified by plasticizers can be derived using the following formula [11]:

$$T_g = T_{gP}c_P + T_{gD}c_D - c_Pc_D(T_{gP} - T_{gD}) \qquad (1)$$

where c is the weight percent concentration and the subscripts P and D refer to the polymer and plasticizer respectively. The polymer of acrylamide (AM) crosslinked with MBAM has a vitrification point of about 188 °C. PEG has a vitrification point lower than 0 °C and PVP-K30 of about 160 °C [12]. The vitrification point of the polymer with various amounts of PEG and PVP was calculated using formula 1 and shown in Table I. It is found that the addition of PEG significantly reduces the vitrification point while PVP has negligible effect.

The flexural strength and elastic modulus of several dried green bodies were measured by three point bending tests and shown in Table I. The standard deviation of the results was within 10% of the average values. Both the strength and elastic modulus of the green bodies decrease with increasing amount of PEG. On the contrary, the addition of PVP increases the elastic modulus of the green bodies. It is also found that the strength and elastic modulus of the green bodies are well correlated with

TABLE I Strength and elastic modulus of the dried green bodies of Al_2O_3

	0.5%PEG	1%PEG	1.5%PEG	1%PVP
Vitrification point (°C)	186	184	182	187
Strength (MPa)	31.5	28.5	22.3	39.7
Elastic modulus (GPa)	10.7	9.4	8.6	13.3

the calculated vitrification point. The results confirm that the addition of PEG can weaken the intermolecular interaction of the gel network and hence improve the flexibility of the green body, while PVP has the opposite effect.

In summary, via comparative studies of glycerine, PEG and PVP, it is found that PEG is an excellent plasticizer capable of reducing the internal stress in the green bodies formed by gelcasting. The addition of PEG into the ceramic suspension makes the gel network softer so that the internal stress in the green bodies is reduced and the crack in the debinding process minimized. It can be concluded that an effective plasticizer for gelcasting using AM and MBAM system must be: (1) a large molecule, (2) a polymer with low vitrification point and (3) not cross-linking with the original polymer network.

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